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Supporting Information

1 Experimental Section

1.1 Materials

Unless otherwise stated, analytical grade solvents and commercially available reagents were used without further purification. All solvents were analytical reagents or better and were degassed prior to use. Anhydrous toluene was distilled from Na/benzophenone under argon flow. Thin-layer chromatography (TLC) employed glass 0.25 mm silica gel plates, the detection of compounds with ultraviolet light ($\lambda =$ 254 nm). Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum ether (bp. 60-90 °C). Gradient flash chromatography was conducted eluting with a continuous gradient from petroleum ether to the dichloromethane or chloroform. All new compounds were characterized by ¹H NMR, ¹³C NMR. The known compounds were characterized by ¹H NMR and ¹³C NMR. The ¹H and ¹³C NMR spectra were recorded on a JNM-ECZ400 400 MHz spectrometer at room temperature. The chemical shifts (δ) were given in part per million relatives to internal tetramethyl silane (TMS, 0 ppm for ¹H), CDCl₃ (77.0 ppm for ¹³C). All chemical shifts (δ) were reported in ppm and coupling constants (J) in Hz. The molecular weight of the polymer acceptor PT-BTP was estimated by high-temperature gel permeation chromatography (HT-GPC) using 1,2,4-trichlorobenzene (TCB) as the eluent at 150 °C and monodispersed polystyrene as the standard. 9'-(2,12-di-tert-butyl-5,9-dioxa-13b-boranaphtho[3,2,1delanthracen-7-yl)-9,9"-diphenyl (PM6) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1Hinden-1-ylidene)malononitrile (IT-2F) were purchased from Solarmer Materials Inc. (2,5-dibromothiophen-3-yl)methanol (3), 3,9-dinonyl-12,13-bis(2-octyldodecyl)-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno[2",3":4',5']thieno[2',3':4,5]pyrrolo[3,2g]thieno[2',3':4,5]thieno[3,2-b]indole-2,10-dicarbaldehyde (7) were synthesized according to the procedures outlined in the literatures, respectively. The synthetic routes

of monomer M1 and polymer acceptor PT-BTP are as follows.



Scheme S1. Synthetic routes of monomer M1 and polymer acceptor PT-BTP.

(2,5-dibromothiophen-3-yl)methyl-1-(dicyanomethylene)-3-oxo-2,3-dihydro-1Hindene-5-carboxylate (6) To the solution of compound 5 (1 g, 2.25 mmol) and malononitrile (0.6 g, 4.5 mmol) in absolute ethanol (20 mL), anhydrous sodium acetate (0.22 g, 2.7 mmol) was added in one portion. The reaction mixture was stirred for 1 h at room temperature. After the completion of the reaction, the reaction mixture was poured into water and acidified with concentrated hydrochloric acid. The mixture was extracted with dichloromethane, and the combined organic layers were dried over MgSO₄. Then, the solvent was evaporated, and the crude was purified via flash column chromatography using dichloromethane as eluent, yielding a yellow solid (0.66 g, 60%). ¹H NMR spectra for compound 6: ¹H NMR (600 MHz, Chloroform-d) δ 8.62 – 8.61 (m, 1H), 8.50 (dd, J = 8.0, 1.5 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.07 (s, 1H), 5.30 (s, 2H), 3.32 (s, 2H); ¹³C NMR (151 MHz, Chloroform-d) δ 196.67, 196.37, 143.40, 136.58, 136.31, 135.90, 131.01, 124.79, 113.00, 111.97, 61.16, 53.48, 45.44, 29.73, 1.05.

Synthesis of (2,5-dibromothiophen-3-yl)methyl (Z)-1-(dicyanomethylene)-2-((10-(((Z)-1-(dicyanomethylene)-5,6-difluoro-3-oxo-1,3-dihydro-2H-inden-2-

ylidene)methyl)-3,9-dinonyl-12,13-bis(2-octyldodecyl)-12,13-dihydro-

[1,2,5]thiadiazolo[3,4-e]thieno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-

g]thieno[2',3':4,5]thieno[3,2-b]indol-2-yl)methylene)-3-oxo-2,3-dihydro-1H-

indene-5-carboxylate (M1) Under the protection of argon, 3,9-dinonyl-12,13-bis(2-octyldodecyl)-12,13-dihydro-[1,2,5]thiadiazolo[3,4-

e]thieno[2",3":4',5']thieno[2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]thieno[3,2-b]indole-2,10-dicarbaldehyde (7) (510 mg, 0.39 mmol, 1.0 equiv.) and both end-capped groups of compound 6 (480 mg, 0.975 mmol, 2.5 equiv.) and IT-2F (224 mg, 0.975 mmol, 2.5equiv.) were dissolved in anhydrous chloroform (45 ml), anhydrous pyridine (1 mL) was then added and the mixture was stirred and refluxed overnight. After cooling to room temperature, the mixture was concentrated to ca. 5 mL and poured into methanol (200 mL) and then filtered. The residue was purified by column chromatography on silica gel using a mixture solvent as eluent (petroleum ether/chloroform) to afford the final product M1 as a dark solid (482 mg, yield: 62%). ¹H NMR spectra for M1: ¹H NMR (600 MHz, Chloroform-d) δ 9.16 (s, 2H), 8.59 – 8.55 (m, 3H), 7.69 (t, J = 7.5 Hz, 3H), 6.95 (s, 1H), 4.97 (s, 2H), 4.72 (d, J = 7.3 Hz, 5H), 3.22 (t, J = 8.1 Hz, 5H), 2.21 (s, 4H), 2.04 (d, J = 13.0 Hz, 4H), 1.90 – 1.83 (m, 8H), 1.38 – 1.35 (m, 10H), 1.28 (d, J = 12.9 Hz, 20H), 1.12 (d, J = 7.7 Hz, 34H), 0.99 - 0.94 (m, 31H). ¹³C NMR (151 MHz, Chloroform-d) & 186.07, 173.35, 153.94, 144.96, 137.85, 136.60, 135.93, 135.21, 133.72, 133.23, 130.93, 129.99, 119.42, 115.11, 114.74, 111.90, 68.08, 59.68, 56.41, 55.26, 38.99, 34.03, 31.94, 31.87, 31.85, 31.32, 30.39, 30.33, 29.92, 29.88, 29.75, 29.64, 29.56, 29.49, 29.46, 29.38, 29.35, 29.32, 29.21, 29.09, 29.00, 26.66, 24.82,

22.70, 22.69, 22.62, 14.14.

Polymerization of PT-BTP In a dry 25 mL two-necked flask, M1 (199.4 mg, 0.10 mmol) and 2,5-bis(trimethylstannyl)thiophene (M2) (41.0 mg, 0.10 mmol) were dissolved in anhydrous toluene (10 mL). After flushing with argon for 10 minutes, $Pd(PPh_3)_4$ (7.6 mg) was added into the flask quickly, the mixture was flushed with argon for another 15 minutes and stirred at 110 °C for 12 hours under argon. Then the reaction mixture was cooled down to room temperature and precipitated into methanol (200 mL). The polymer was collected by filtration through a Soxhlet extractor and then subjected to Soxhlet extractions with methanol, acetone, and chloroform each for 12 hours, respectively. Then the chloroform fraction was concentrated and precipitated with methanol, the dark solid was obtained. (156 mg, 65% yield).

1.2 Characterization of Photovoltaic Materials

Ultraviolet-visible near-infrared (UV-vis-NIR) absorption spectra were recorded with a Perkin-Elmer Lambda 365 UV-Vis spectrophotometer from 300 nm to 1100 nm. Electrochemical properties were studied by cyclic voltammetry (CV). CV was performed on a CS350H electrochemical workstation with a conventional threeelectrode system in a tetrabutylammonium hexafluorophosphate (*n*-Bu4NPF6, 0.1 M) acetonitrile solution at a scan rate of 100 mV s⁻¹. A glassy carbon disc coated with sample film was used as the working electrode. A Pt wire was used as the counter electrode and Ag/AgCl was used as the reference electrode. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels ($E_{\rm HOMO}/E_{\rm LUMO}$) can be calculated from the onset oxidation/reduction potentials ($\phi_{\rm ox}/\phi_{\rm red}$ + 4.8 - $\phi_{\rm Fe/Fe}^+$) (eV), where $\phi_{\rm Fe/Fe}^+$ is the redox potential of ferrocene/ferrocenium (Fc/Fc+) couple in the electrochemical measurement system, and the energy level of Fc/Fc+ was taken as -4.8 eV below the vacuum level.

1.3 Device Fabrication and Testing

The small area solar cell devices were fabricated with a conventional structure of Glass/ITO/PEDOT: PSS/active layer/PFN-Br/Ag. Pre-patterned ITO-coated glass was used as the substrate. It was cleaned by sequential ultrasonication in soap-deionized water, deionized water, acetone and isopropanol for 15 min at each step. The washed substrates were further UV-treated in an ultraviolet-ozone chamber for 15 min. Aqueous solution of PEDOT:PSS (poly(3,4-ethylene dioxythiophene): poly(styrene sulfonate)) was filtered through a 0.45 µm poly(tetrafluoroethylene) (PTFE) filter and spin-coated onto the ITO substrate at a spinning rate of 3500 rpm for 30 s and then baked in air at 150 °C for 15 min. A mixture of PM6:PT-BTP (1:1.2, w/w) was dissolved in CF solvent (16mg mL⁻¹ in total, with 1.5 vol% 1-chloronaphthalene as additive). Then, these solutions were spin-coated on the PEDOT:PSS layer to form active layer of around 100nm. The post-processing is then further optimized, as detailed in the following sections. The thickness of the photoactive layer is measured by a surface profiler (Alpha-Step 500, KLA-Tencor, USA). The PFN-Br was dissolved in methanol with concentration of 0.5 mg mL⁻¹ and then deposited the top of the active layer. Finally, top Ag electrode of 100 nm thickness was evaporated in a vacuum onto the cathode buffer layer at a pressure under 5×10^{-6} mbar. The typical active area of the investigated devices was 5 mm². The current-voltage characteristics of the solar cells were measured under AM 1.5 G irradiation on an Enli Solar simulator (100 mW cm⁻²). Before each test, the solar simulator was calibrated with a standard single-crystal Si solar cell (made by Enli Technology Co., Ltd., Taiwan, calibrated by The National Institute of Metrology (NIM) of China). The external quantum efficiency was measured by a Solar Cell Spectral Response Measurement System QE-R3011 (Enli Technology Co., Ltd.). A calibrated silicon detector was used to determine the absolute photosensitivity at different wavelengths.

1.4 Morphological and Physical Measurements

Atomic force microscopy (AFM) measurements: All samples were prepared by spincoating onto ITO/PEDOT:PSS substrates. The atomic force microscopy (AFM) measurement was investigated on a Dimension Icon AFM (Bruker) in a tapping mode. The root-mean-square (RMS) roughness values of the surface AFM images are averaged based on five times testing on different areas for each sample.

Transmission Electron Microscopy (TEM) Characterization: Transmission electron microscopy (TEM) was performed on a Tecnai G2 F20 S-TWIN instrument at 200 kV accelerating voltage.

Space charge limited current (SCLC) measurements: The charge carrier mobilities of the binary films were measured using the space-charge-limited current (SCLC) method. The structure of hole-only devices was Glass/ITO/PEDOT:PSS/Active layer/MoO3 (10 nm)/Ag (100 nm). For the electron-only devices, the structure was Glass/ITO/ZnO/Active layer/PFN-Br/ Ag (100 nm). The reported mobility data are average values over the two cells of each sample at a given film composition. The device characteristics were extracted by modeling the dark current under forwarding bias using the SCLC expression described by the Mott-Gurney law: $J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu \frac{V^2}{I^3}$

Here, $\varepsilon_r \approx 3$ is the average dielectric constant of the blend film, ε_0 is the permittivity of the free space, μ is the carrier mobility, L is the thickness of the film, and V is the applied voltage.

Transient photocurrent (TPC) measurements: Relevant solar cells were excited with a 405 nm laser diode. The transient photocurrent response of the devices at short circuit condition to a 200 μ s square pulse from the LED with no background illumination. The current traces were recorded on a Tektronix DPO3034 digital oscilloscope by measuring the voltage drop over a 5-ohm sensor resistor in series with the solar cell.

DC voltage was applied to the solar cell with an MRF544 bipolar junction transistor in a common collector amplifier configuration.

Transient photocurrent (TPV) measurements: In the TPV measurements, a 405 nm laser diode was used to keep the organic solar cells in the V_{oc} conditions. Measuring the light intensity with a highly linear photodiode and driving the laser intensity with a waveform generator (Agilent 33500B) at one sun. Moreover, a small perturbation was induced with a second 405 nm laser diode. The intensity of the short laser pulse was adjusted to keep the voltage perturbation below 10 mV. After the pulse, the voltage decays back to its steady state value in a single exponential decay.

FTPS-EQE spectra measurements: The FTPS measurements were recorded using a Bruker Vertex 70 Fourier-transform infrared (FTIR) spectrometer, equipped with a quartz tungsten halogen lamp, a quartz beam-splitter, and an external detector option. A low noise current amplifier (Femto DLPCA-200) was used to amplify the photocurrent produced on the illumination of the photovoltaic devices with light modulated by the FTIR. The output voltage of the current amplifier was fed back into the external detector port of the FTIR. The photocurrent spectrum was collected by FTIR's software.

Electroluminescence Measurement: The EL signature was collected with a monochromator and detected with an InGaAs detector. The data collection range is 700-1300 nm.

Light stability testing: The corresponding solar cells under MPP were tested in a nitrogen glovebox at room temperature. The devices were illuminated using a light-emitting diode (LED) array (its light intensity was ~1 Sun) and the power output was measured continuously using a source meter controlled by a program written in LabVIEW.

2. Supplemental Fig.s and Tables



Fig. S1 The chemical structure of PYF-T.



Fig. S2 ¹H NMR spectrum of compound 5.



Fig. S3 ¹³C NMR spectrum of compound 5.



Fig. S4 ¹H NMR spectrum of compound M1.



Fig. S5 ¹³C NMR spectrum of compound M1



Fig. S6 ¹H NMR spectrum of PT-BTP.



Fig. S7 The molecular mass of PT-BTP was determined by high-temperature gel permeation chromatography using 1,2,4-trichlorobenzene as the eluent at 150 $^{\circ}$ C.

PSMASolutiona λ_{max} Filmb λ_{max} Filmb λ_{edge} E_{g}^{opt} LUMO d(eV)HOMOd(eV)PT-BTP744nm811nm920nm1.35-3.63-5.73

Table S1. Summary of optical properties, and electronic energy levels of PT-BTP

^aAbsorption peak measured in chloroform solution.

^bAbsorption peak measured in film state.

^cOptical bandgap estimated from the onset wavelength of the film-state absorption.

^dEnergy level measured by electrochemical cyclic voltammetry.



Fig. S8 Normalized UV-vis-NIR absorption spectra of PT-BTP in the film.



Fig. S9 Cyclic voltammogram (CV) curves of PT-BTP on glassy carbon electrode in $0.1 \text{ mol } L^{-1} \text{ Bu}_4 \text{NPF}_6$ acetonitrile solution at a scan rate of 100 mV s⁻¹.



Fig. S10 The dark *J-V* characteristics of PT-BTP based electron-only devices. The solid lines represent the best fitting using SCLC model.



Fig. S11 *J-V* curves of the OSCs based on PM6:PT-BTP blends with different donor/acceptor weight ratios, measured under the illumination of AM 1.5 G at 100 mW cm⁻².

Table S2 Photovoltaic parameters of the OSCs based on PM6:PT-BTP blends with different donor/acceptor weight ratios, measured under the illumination of AM 1.5 G at 100 mW cm⁻².

| Active layer | D:A | $V_{\rm oc}$ [V] | $J_{\rm sc} [{\rm mA~cm}^{-2}]$ | FF [%] | $PCE(PCE^a)$ [%] |
|--------------|-------|------------------|---------------------------------|--------|------------------|
| | 1:1.2 | 0.85 | 22.60 | 60.06 | 11.56 (11.08) |
| PM6:PT-BTP | 1:1.5 | 0.85 | 24.39 | 58.71 | 12.13 (11.45) |
| | 1:1.8 | 0.83 | 22.82 | 54.69 | 10.46 (10.10) |

^{*a*}The values in the square bracket are the average PCE obtained from eight devices.



Fig. S12 *J-V* curves of the OSCs based on PM6:PT-BTP blends with different amounts of 1-chloronaphthalene (CN) and thermal annealing at 100 °C for 10 minutes, under the illumination of AM 1.5 G at 100 mW cm⁻².

Table S3 Photovoltaic parameters of the OSCs based on PM6:PT-BTP blends with different amounts of 1-chloronaphthalene (CN) and thermal annealing at 100 °C for 10 minutes, under the illumination of AM 1.5 G at 100 mW cm⁻².

| Active layer | Additive CN [%] | $V_{\rm oc}$ [V] | $J_{\rm sc}$ [mA cm ⁻²] | FF [%] | PCE (PCE ^{<i>a</i>})[%] |
|--------------|--------------------|------------------|-------------------------------------|--------|-----------------------------------|
| PM6:PT-BTP | 2.5 | 0.79 | 20.58 | 44.16 | 7.18 (7.13) |
| | 2 | 0.84 | 23.09 | 56.81 | 11.01 (10.87) |
| | 1.5 | 0.85 | 24.39 | 58.71 | 12.13 (11.45) |
| | 1 | 0.81 | 22.53 | 58.28 | 10.64 (10.37) |
| | 0.5 | 0.80 | 22.73 | 51.85 | 9.43 (9.23) |

 $^{\alpha}$ The values in the square bracket are the average PCE obtained from eight devices.



Fig. S13 (A) The structures of PT-BTP and Y2F-ET. (B) *V*oc, (C) FF, (D) J_{SC} and (E) PCE of the relevant photoaged devices, the parameters are measured under the simulated illumination of AM 1.5 G at 100 mW cm⁻².



Fig. S14 Normalized UV-vis-NIR absorption spectrum of the as-cast and optimized PM6:PT-BTP blend films.



Fig. S15 The dark *J-V* characteristics of PM6:PT-BTP based electron-only devices. The solid lines represent the best fitting using SCLC model. The inset mobility data are average values based on eight devices with the same thickness.



Fig. S16 The dark *J-V* characteristics of PM6:PT-BTP based hole-only devices. The solid lines represent the best fitting using SCLC model. The inset mobility data are average values based on eight devices with the same thickness.



Fig. S17 The measured J_{sc} of the as-cast and optimized devices as a function of light intensity (symbols), together with linear fits to the J_{sc} data (dash lines).



Fig. S18 The derivative of EQE with respect to energy for (A) as-cast and (B) optimized devices.